

Magnetic Field Dependent Coherent Polarization Echoes in Glasses

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(Dated: February 1, 2008)

The unexpected finding of a strong magnetic field dependence of the dielectric properties of insulating glasses at very low temperatures has been a puzzling problem since its discovery. Several attempts have been made to explain this striking phenomenon. In order to obtain information on the origin of the magnetic field effects we have studied coherent properties of atomic tunneling systems in glasses by polarization echo experiments in magnetic fields. Our results clearly favor a model based on the assumption that nuclear quadrupoles play a crucial role for the observed magnetic field dependence.

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PACS numbers: 61.43.Fs, 64.90.+b, 77.22.Ch

I. INTRODUCTION

The absence of first order magnetic field effects in insulating materials free of magnetic moments can be concluded from basic principles. Since the magnetic field is described by an axial vector and the electrical polarization by a polar vector, a linear magnetic field dependence of the dielectric properties of pure non-magnetic insulators can be ruled out. Therefore, it is very surprising that strong magnetic field effects were discovered recently in low-frequency dielectric susceptibility measurements on certain multi-component glasses at very low temperatures.^{1,2,3,4,5} In particular, a non-monotonic variation of the dielectric constant and of the dielectric loss was observed with increasing magnetic field.

Since the low-temperature dielectric properties of insulating glasses are governed by atomic tunneling systems it was speculated on a direct coupling of magnetic fields to tunneling systems. Two models have been proposed that relate the magnetic field dependence to the Ahanorov-Bohm phase of a charged particle moving along a closed loop.^{6,7}

In polarization echo experiments at radio frequencies it has already been demonstrated that tunneling systems in glasses couple directly to magnetic fields.⁸ Surprisingly, the amplitude of two-pulse echoes in a-BaO-Al₂O₃-SiO₂ (BAS) was found to depend strongly on the applied magnetic field showing a non-monotonic field variation. Since in polarization echo experiments only the properties of tunneling states are probed these findings prove that indeed the tunneling systems themselves are involved in the magnetic field effect. Furthermore, the character of certain features observed in these echo experiments indicate that nuclear magnetic moments might play an important role.

To explain the magnetic field effects in echo experiments a coupling to nuclear spins has recently been discussed theoretically.⁹ The model worked out in this publication is based on the assumption that the levels of tunneling particles with non-zero nuclear quadrupole moment exhibit a quadrupole splitting, which is different in the ground state and in the excited state. Magnetic

fields cause an additional Zeeman splitting of these levels giving rise to interference effects. In turn, these effects cause the non-monotonic magnetic field variation of the echo amplitude.

In this communication we present the results of polarization echo experiments on four different glasses in magnetic fields investigated under different experimental conditions. Furthermore, we discuss briefly the models developed to explain the magnetic field effects and compare their predictions with our experimental findings.

II. THEORETICAL BACKGROUND

In the following sections we briefly introduce the tunneling model, which is the generally accepted basis for the description of the low-temperature properties of amorphous solids. In addition, we discuss the physics of polarization echoes in glasses, and the theoretical approaches to explain the magnetic field dependence of the dielectric properties of non-magnetic insulating glasses.

A. Tunneling Model

Atomic tunneling states give rise to an important contribution to the internal energy of glasses at low temperatures. Most properties of amorphous solids are strongly influenced by these additional degrees of freedom. Two prominent examples are the linear specific heat and the logarithmic temperature dependence of the sound velocity.^{10,11} A phenomenological description of the low-temperature properties of glasses is provided by the so-called ‘tunneling model’, that has been proposed independently by Phillips¹² and Anderson et al.¹³ in 1972. A central assumption of this model is that atoms or small groups of atoms are not located in well-defined potential minima, but move between two energetically almost equivalent adjacent positions separated by a potential barrier. Such a configuration can be described by a ‘particle’ moving in a double-well potential. In this approximation the single wells are considered as harmonic

and identical, but may differ in their depth. This difference is usually referred to as the asymmetry energy Δ . These particles have vibrational states in each single well, separated by the energy E_0 .

At low temperatures, i.e., for $k_B T \ll E_0$, higher vibrational levels are not excited and can be omitted in our further discussion. The ground state is split into two levels by the tunneling motion. Therefore, tunneling systems in glasses are often referred to as *two-level systems*. In addition to the classical potential difference Δ , the quantum mechanical tunnel splitting Δ_0 contributes to the ground state splitting E given by

$$E = \sqrt{\Delta^2 + \Delta_0^2}. \quad (1)$$

Applying the WKB approximation the tunnel splitting can be calculated approximately. Neglecting prefactors of the order of unity one finds

$$\Delta_0 \approx E_0 e^{-\lambda}. \quad (2)$$

Roughly speaking the tunnel splitting Δ_0 is given by the vibrational energy E_0 of the particle multiplied by the probability $\exp(-\lambda)$ for tunneling. The so-called tunneling parameter $\lambda = d\sqrt{2mV}/2\hbar$ reflects the overlap of the wave functions of the particle at the two sides of the potential barrier.

As a consequence of the irregular structure of glasses, the characteristic parameters of the tunneling states are widely distributed. In the tunneling model it is assumed that the asymmetry energy Δ and the tunnel parameter λ are independent of each other and uniformly distributed as

$$P(\lambda, \Delta) d\lambda d\Delta = \bar{P} d\lambda d\Delta, \quad (3)$$

where \bar{P} is a constant. Using this particular distribution function many low-temperature properties of glasses can be explained even quantitatively. An equivalent description of the low-temperature properties of glasses is given by the so-called ‘soft potential model’¹⁴ that uses a more general form of the atomic potentials and different distribution functions. It allows reliable predictions even well above 1 K. In comparison with the tunneling model the soft potential model leads to a slightly different distribution of the tunneling parameter, but for the properties below 1 K it yields the same predictions.

Tunneling systems couple to their environment by interaction with phonons and photons. External elastic or electric fields produce changes of the asymmetry energy Δ and lead to relaxation processes. The coupling to external fields also causes resonant processes like resonant absorption and stimulated emission. Both, resonant and relaxational contributions determine the dynamic response of the two-level systems. For a tunneling system with electric dipole moment \mathbf{p} in an electric field $\mathbf{F}(t)$ the Hamiltonian in the orthogonal basis of the eigenfunctions ψ_- and ψ_+ of ground and excited state is given

by

$$H = \frac{1}{2} \begin{pmatrix} E & 0 \\ 0 & -E \end{pmatrix} + \frac{1}{E} \begin{pmatrix} \Delta & -\Delta_0 \\ -\Delta_0 & -\Delta \end{pmatrix} \mathbf{p} \cdot \mathbf{F}(t) \quad (4)$$

Using this Hamiltonian the coherent dynamics of tunneling systems can be formulated.

B. Polarization Echoes in Glasses

At very low temperatures the relaxation of the tunneling systems becomes so slow that coherent phenomena like polarization echoes become observable in insulating glasses. Depending on the sequence and phase of the exciting pulses, different physical properties of the tunneling systems can be studied.^{15,16} Here we focus on one particular kind of experiment, the so-called spontaneous echo (or two-pulse echo) which is generated by two short microwave pulses separated by the delay time t_{12} . The macroscopic polarization produced by the first microwave pulse vanishes rapidly due to the distribution of parameters of the tunneling systems in glasses. This phenomenon is similar to the well-known free induction decay observed in nuclear magnetic resonance experiments.

Neglecting relaxation processes and spectral diffusion¹⁷ resulting from the interaction of neighboring tunneling systems, the phase of the individual tunneling systems develops freely between the two exciting pulses. The second pulse causes an effective time reversal of the development of the phase of the tunneling systems. The initial macroscopic polarization of the glass is recovered at the time t_{12} after the second pulse. In analogy to the two-pulse echo in magnetic resonance experiments this phenomenon is referred to as the spontaneous echo. Due to the broad distribution of the parameters of the two-level systems in glasses, the description of polarization echoes in glassy materials is somewhat more involved than in the simple case of diluted paramagnetic spin systems. A detailed and general theoretical discussion of spontaneous echoes in glasses has been given by Gurevich et al.¹⁸. A few results of this theory relevant to the experiments presented here, will be summarized in the following.

The amplitude of the echo depends on the pulse area, i.e., the length of the exciting pulses times the field strength of the microwave. A maximum of the echo amplitude is observed for pulses with pulse areas $\Omega t_{p1} \approx \pi/2$ and $\Omega t_{p2} \approx \pi$, where t_{p1} and t_{p2} denote the duration of the first and second pulse, respectively, and Ω the effective Rabi frequency given by

$$\Omega = \sqrt{\Omega_R^2 + \omega_d^2}. \quad (5)$$

Here $\omega_d = \omega_r - \omega$ signifies the difference between the frequency ω of the microwave and the resonance frequency $\omega_r = E/\hbar$ of the tunneling systems. The quantity

Ω_R represents the Rabi frequency of systems at $\omega_d = 0$ and is given by

$$\Omega_R = \frac{1}{\hbar} \frac{\Delta_0}{E} \mathbf{p} \cdot \mathbf{F}_0, \quad (6)$$

where $|\mathbf{F}_0|$ is the field strength of the exciting microwave pulse. Neglecting again any kind of phase disturbing processes, the amplitude of spontaneous echoes in glasses is expected to vary as¹⁸

$$A(t) = A_0 \tanh\left(\frac{E}{2k_B T}\right) \text{Im} \left\{ e^{i\omega t} \int_0^1 \cos^4 \Theta \, d\Theta \int_0^1 \frac{\eta \, d\eta}{\sqrt{1-\eta}} \right. \\ \left. \int_{-\infty}^{+\infty} \frac{1}{\Omega^3} \left[\sin(\Omega t_{p1}) - 2i \frac{\omega_d}{\Omega} \sin^2\left(\frac{\Omega t_{p1}}{2}\right) \right] \right. \\ \left. \sin\left(\frac{\Omega t_{p2}}{2}\right) e^{i\omega_d(t-2t_{12})} d\omega_d \right\}, \quad (7)$$

with $\eta = \Delta_0/E$, and Θ representing the angle between \mathbf{p} and \mathbf{F}_0 . The amplitude A_0 is determined by the number of tunneling states, their dipole moment and the field strength of the microwave.

At finite temperatures, thermal relaxation processes and spectral diffusion weaken the coherence of the ensemble of resonant tunneling systems. Thus the echo amplitude is increasingly reduced with growing delay time t_{12} . Since thermal relaxation processes and spectral diffusion are strongly temperature dependent, coherent polarization echoes in glasses can be observed only at very low temperatures, typically below 100 mK. We shall not discuss these processes here since they are not of importance for the phenomena reported here. However, we like to point out that the echo amplitude is proportional to the number of tunneling systems which are in resonance with the exciting microwave pulse and do not lose their phase coherence during the time $2t_{12}$.

C. Coupling to Magnetic Fields

Recently, several models have been developed with the aim to explain the coupling of magnetic fields to atomic tunneling systems in disordered solids. Here we discuss first two models that focus on the description of the dielectric constant of glasses in magnetic fields. Then we consider the model that aims to explain the magnetic field effects observed in polarization echo experiments.

1. Mexican-hat Model

To describe the non-monotonic magnetic field dependence of the dielectric susceptibility of multi-component glasses, Kettemann et al.⁶ investigated the properties of tunneling systems exhibiting the peculiarity that the tunneling particle can move along different paths to go from

one potential minimum to the other thus forming a closed tunneling loop. As a simple example they considered a Mexican-hat type potential with two equivalent minima in the brim. At zero magnetic field the tunneling probability is equal for either direction of tunneling. However, in a magnetic field perpendicular to the plane of the tunneling loop the time inversion symmetry is broken and the probability for tunneling is in general not equal anymore for the two directions of revolution. As a result the tunnel splitting Δ_0 becomes a periodic function of the magnetic flux ϕ threading through the loop, i.e., $\Delta_0(\phi) = \Delta_0(\phi=0) \cos(\pi\phi/\phi_0)$, where $\phi_0 = h/e$ represents the elementary flux quantum. Consequently, the energy spectrum of the tunneling systems varies periodically with the applied magnetic field and so does the dielectric constant of the glass.

In this model, maxima in the dielectric constant are expected at $\phi/\phi_0 = (2n+1)/2$, with $n = 0, 1, 2, \dots$. The magnetic field required to reach the first maximum of the dielectric constant turns out to be of the order of 10^5 T if the tunneling systems carry an elementary charge and have atomic dimensions. However, experimentally the first maximum was found at about 100 mT. This clear contradiction was interpreted by Kettemann et al. as an indication that not individual tunneling systems are responsible for the magnetic field effect but a large number of strongly coupled systems with a much larger effective charge and a larger effective loop radius. Although evidence for interactions between tunneling systems in glasses have been found in several experiments at very low temperatures^{19,20,21,22,23,24} it remains an open question whether clusters of 10^5 coherently moving tunneling systems exist in glasses.

No specific predictions were made for echo experiments in this work. However, the predicted periodical variation of the tunnel splitting should be observable since Δ_0 enters in several quantities relevant in echo experiments. For example, one such quantity is the Rabi frequency.

2. Pair Model

A somewhat different point of view had been taken by Würger⁷, who considered the properties of pairs of interacting tunneling systems in magnetic fields. Suppose that there are two neighbored interacting tunneling systems of similar energy with tunneling paths along different directions. In this case the interaction between the tunneling particles would lead to a bending of the tunneling paths and to a correlation of the tunnel motion of the two systems. It is conceivable that a closed loop is formed along which the effective charge of the tunneling systems is transported. The important difference to the Mexican-hat model is that the level scheme of a coupled pair differs from that of a two-level system. Two weakly coupled two-level systems of similar energy splitting have four levels, the two in the middle being almost degenerate. The separation of the two levels in the middle will periodically vary as a function of magnetic flux through the effective loop.

Within this approach, the splitting of the two almost degenerate levels is given by the relation $E_p = \sqrt{\delta^2 + \zeta^2}$, with δ representing the difference in the energy splitting of the two coupled tunneling systems $\delta = E_1 - E_2$, and ζ denoting their magnetic field dependent variation $\zeta = 2\Delta_0 \sin(\pi\phi/\phi_0)$. The important feature of this model is that the relative change of the small splitting E_p caused by magnetic fields is much larger than the relative variation of the energy splittings E_1 and E_2 of isolated tunneling systems. Within this model the magnetic field variation $\Delta\varepsilon$ of the dielectric constant ε is approximately given by

$$\Delta\varepsilon \propto \frac{1}{B} \left[1 - \cos \left(\frac{2\pi\Gamma\phi^2}{\phi_0^2} \right) \right], \quad (8)$$

with $\Gamma = 2\pi\Delta_0^2/(\hbar\omega pF)$. Here, B denotes the magnetic field, ω the frequency of measurement and F the amplitude of the applied ac field. Inserting typical values of low-frequency measurements one can estimate the parameter Γ to be $\Gamma \approx 10^{10}$. Therefore, the oscillation period is determined by an effective flux quantum $\phi_0/\sqrt{\Gamma} \approx 10^{-5}\phi_0$, which appears to be of the right order of magnitude for describing the observed non-monotonic magnetic field variation of ε . However, it should be pointed out, that this explanation relies unambiguously on the presence of coupled pairs of tunneling systems with almost identical energy splitting and exhibiting a correlated tunneling motion with an effective tunneling loop. It is unclear at this point how large the fraction of tunneling systems in glasses is, having the required properties.

As stated above, the pair model aims to describe the dielectric susceptibility data and no specific predictions were made for polarization echo experiments.⁷ Nevertheless, one would certainly expect a pronounced frequency dependence since the parameter Γ is inversely proportional to the measuring frequency.

3. Nuclear Quadrupole Model

Very recently, an alternative explanation for the magnetic field effects of the dielectric properties of insulating glasses has been suggested.⁹ The central assumption of this model is, that the nuclear properties of the tunneling systems are responsible for the observed phenomena. Nuclei with a spin $I \geq 1$ also carry a nuclear quadrupole moment Q . Because of electric field gradients present in glasses, both, the ground state and the excited state of tunneling systems containing nuclei with a quadrupole moment, will exhibit a quadrupole splitting $\hbar\omega_Q$, that is generally different for the two levels. Magnetic fields couple to the nuclear magnetic dipole moment and lead to a nuclear Zeeman splitting $\hbar\omega_L = g\mu_N B$. Here g represents the g -factor of the nuclei and μ_N the nuclear magneton. The behavior of such systems in polarization echo experiments depends on the relative magnitude of the two energies. At low magnetic fields ($\hbar\omega_L \ll \hbar\omega_Q$) the amplitude of a two-pulse polarization echo for nuclei with

half-integer spin and $I \geq 3/2$ should approximately be given by⁹

$$A(t_{12}, \omega_L) = A(t_{12}, \infty) \left\{ 1 - a + b_{1/2} \int_0^1 p(x) \cos \left[\sqrt{x^2 + (I + 1/2)^2(1 - x^2)} \omega_L t_{12} \right] dx + \sum_{\beta > 1/2} b_\beta \int_0^1 p(x) \cos (2\beta \omega_L t_{12} x) dx \right\} \quad (9)$$

where a and b_β are coefficients depending on the nuclear spin, and $A(t_{12}, \infty)$ denotes the echo amplitude in the limit of high magnetic fields. The parameter x represents the projection of the quantization axis of the magnetic moments onto the quadrupole axis and $p(x)$ is its normalized distribution. The sum runs over $\beta = 1/2, \dots, I$ for half-integer spins.²⁵ For $B = 0$ the amplitude of the echo is given by $A(t_{12}) = A(t_{12}, \infty)[1 - a + \sum_\beta b_\beta]$. Compared to the amplitude caused by an ensemble of simple two-level systems it is reduced by the fraction $(a - \sum_\beta b_\beta)$, which arises from the interference of different quadrupole levels.²⁶ At small magnetic fields the degeneracy of the nuclear magnetic levels is lifted and causes an additional line broadening due to additional transition energies. The non-monotonic variation of the echo amplitude with the magnetic field results from the magnetic field dependence of the distribution of nuclear spin levels and the interference of their contributions to the signal. The first minimum of (9) is expected to occur roughly at $\omega_L t_{12} \approx 0.5\pi$.²⁷ Inserting the expression for the nuclear Zeeman energy this condition leads to

$$B_{\min} t_{12} \approx \frac{0.5 \pi \hbar}{g\mu_N}. \quad (10)$$

Thus the nuclear quadrupole model predicts that the position of the minimum only depends on the nuclear magnetic dipole moment of the tunneling particle. As a consequence echo experiments are expected to reveal interesting information on the material dependence of the magnetic field phenomena in glasses. It is noteworthy, however, that the tunneling systems in glasses are probably not caused by the motion of single atoms, but are likely to involve the correlated motion of small atomic clusters. In this case, the interpretation of the non-monotonic variation of the echo amplitude with magnetic field is obviously more complex.

At large magnetic fields ($\hbar\omega_L \gg \hbar\omega_Q$) the situation simplifies significantly and reduces to the case of a simple two-level system, because the nuclear Zeeman splitting leads to equally spaced spin levels for both, the ground states and the excited states of the tunneling systems. According to the nuclear quadrupole model⁹ the variation of the two-pulse echo amplitude at large magnetic fields should approximately be given by

$$\frac{A(B)}{A(B \rightarrow \infty)} \approx 1 - \frac{B_0^2}{B^2}, \quad (11)$$

where the constant B_0 marks the magnetic field at which $\hbar\omega_L \approx \hbar\omega_Q$. Note that at high fields the normalized amplitude does not depend on the delay time t_{12} whereas at low fields a delay time dependence is expected. From the magnetic field strength of the transition from the low-field to the high-field regime it is possible to estimate the magnitude of the nuclear quadrupole splitting with the help of this model.

III. EXPERIMENTAL TECHNIQUE

The experiments were performed in a ^3He - ^4He dilution refrigerator in order to reach temperatures down to about 10 mK, which are necessary to study coherent polarization echoes in glasses. The cooling power of the apparatus was sufficient to overcome the heat input by the two coaxial cables carrying the r.f. signals and by the r.f. power dissipated in the experiment itself. All r.f. lines inside the refrigerator were semi-rigid coaxial cables with low insertion loss up to the GHz range. Inside the vacuum enclosure of the refrigerator the coaxial cables are made from superconducting niobium in order to keep the heat input by thermal conduction as low as possible. Thermalization of the niobium cables is performed at the still with home made strip-line devices on a single-crystal sapphire substrate. The temperature was measured by an Au:Er susceptibility thermometer and a carbon resistor, both attached to the mixing chamber of the apparatus.

1. Echo Generation and Detection

The echo experiments were performed in a re-entrant microwave resonator attached to the mixing chamber of the dilution refrigerator. The resonator was made from gold plated oxygen free copper. The sample discs with a thickness of about 0.5 mm and a diameter of 8 mm were mounted in the region between the center post and the bottom of the resonator. In this area a large portion of the electric field component of the resonator is concentrated and, because of the diameter (8 mm) of the center post, the field was rather homogeneous. The r.f. signal was inductively coupled into the resonator by a loop which could be rotated in order to adjust the degree of coupling. Two modes, the ground mode at 1 GHz and the first overtone at 4.6 GHz were used in our experiments.

The echo signal was picked up by a second loop in the resonator and was pre-amplified by approximately 43 dB using a helium-cooled microwave amplifier located in the helium bath outside the vacuum chamber. The signal was mixed outside the cryostat with a reference signal with the same frequency. The demodulated signal was further amplified by a video amplifier and digitized by a fast digital oscilloscope. Depending on the experiment 1000 to 10000 subsequent echo cycles were digitally averaged in order to reach an acceptable signal to noise ratio.

The r.f. signal was generated by a microwave synthesizer, split into two parts and fed into the receiver and

transmitter branch. The latter consisted of a variable attenuator, a phase shifter, and a p - i - n diode switch used to shape the microwave pulses with an on/off transit time of about 15 ns. The TTL control signals of the diode switch were provided by a digital pulse and delay generator.

Phase sensitive detection has two advantages for our experiment: Firstly, sensitivity is increased by 3 dB because all noise in the quadrature component of the signal is suppressed. Secondly, the output of a phase sensitive detector is bipolar, meaning that the mean value of noise of the detector signal vanishes. In a conventional rectifying ('square law') detector the noise output is unipolar and will therefore average to a finite value. Furthermore, mixing of the bipolar random noise signal with the fixed-polarity echo signal in a rectifying detector would lead to a nonlinear amplitude dependence of the averaged echo at low signal levels.

2. Magnetic Field Generation

In most experiments discussed, here the magnetic field was generated by a home-made superconducting magnet consisting of about 1000 m NbTi wire wound around a stainless steel cylinder with a 22 mm drill-hole and 64 mm in length. The wire was fixed with a thick layer of epoxy (Stycast 2850 FT). The coil was attached to the mixing chamber of the dilution refrigerator and the sample was placed in the middle of the cylinder. The homogeneity of the magnetic field was estimated to be better than 5×10^{-3} . The maximum current through the coil was about 2 A corresponding to a magnetic field strength of 0.46 T. The operation of the magnet at constant field had no noticeable influence on the performance of the cryostat. However, whenever the magnetic field was altered, the temperature of the sample holder increased significantly due to eddy currents, and, after reaching a constant magnetic field, it was slowly relaxing back to the mixing chamber temperature. For experiments at higher fields we used a standard superconducting solenoid with a field range up to 5 T, which was installed at the mixing chamber of our cryostat.

3. Samples

Four different insulating glasses were investigated, namely the two commercially available multi-component glasses BK7 and Duran, the multi-component glass a-BaO-Al₂O₃-SiO₂ (BAS), and vitreous silica containing 1200 ppm OH⁻ (Suprasil I). The main components of these glasses are listed in Table I as determined by atomic emission spectroscopy.²⁸ In addition, in Table II we have listed for the relevant elements, the nuclear spins, the quadrupole moments of the isotopes with non-zero quadrupole moment, and the natural abundance of these isotopes.

Since we were concerned about effects caused by magnetic impurities present in the samples we performed magnetization measurements in a SQUID magnetometer

TABLE I: Mole fraction of the constituents of the four glass samples BAS, BK7, Duran and Suprasil I as determined by atomic emission spectroscopy.²⁸

		BAS	BK7	Duran	Suprasil I
SiO ₂	(%)	72.7	74.8	83.4	100
B ₂ O ₃	(%)	0.72	9.6	11.6	0
Al ₂ O ₃	(%)	8.8	0.03	1.14	0
Na ₂ O	(%)	0.28	10.1	3.4	0
K ₂ O	(%)	0.064	4.7	0.41	0
BaO	(%)	17.0	0.76	0.005	0

TABLE II: Natural abundance, nuclear spin I and nuclear quadrupole moment Q of isotopes with $I > 1/2$ present in the glass samples.

	abundance (%)	I	g	Q (barn)
¹⁰ B	19.9	3	0.60	0.08
¹¹ B	80.1	3/2	1.79	0.04
¹⁷ O	0.05	5/2	-0.76	-0.03
²⁷ Al	100	5/2	1.46	0.14
²³ Na	100	3/2	1.48	0.11
³⁹ K	93.3	3/2	0.26	0.06
⁴¹ K	6.7	3/2	0.14	0.07
¹³⁵ Ba	6.59	3/2	0.56	0.16
¹³⁷ Ba	11.23	3/2	0.62	0.25

to determine the amount of magnetic impurities. Fig. 1 shows the result of such measurements on BK7 and Duran. Although these two glasses have a very similar composition, the change in magnetization and thus the amount of magnetic impurities differ by roughly a factor

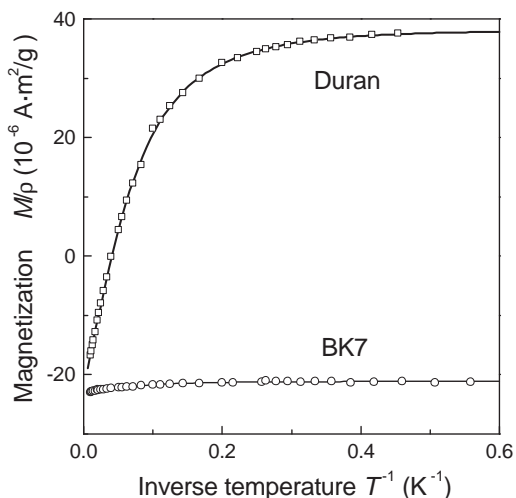


FIG. 1: Magnetization of BK7 and Duran as a function of the inverse temperature. The measurements were carried out in a field of 5.5 T.

of twenty. We conclude from this measurement that the BK7 sample contained about 5 ppm of magnetic impurities with a g -factor of $g \approx 2$ and a total spin of $J = 5/2$, while in Duran about 120 ppm magnetic impurities were found with $g \approx 2$ and $J \approx 5/2$.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

We have studied the influence of magnetic fields on the amplitude of coherent polarization echoes depending on various parameters such as frequency, delay time, electric field strength and temperature. As we will see, the experimental results allow to distinguish between the different models discussed above.

A. Spontaneous Echoes in Magnetic Fields

1. Electric Field Dependence

Let us first discuss the dependence of the echo amplitude on the electric field strength of the exciting microwave pulses. In all experiments the widths of the pulses were kept constant, being $t_{p1} \approx 100$ ns and $t_{p2} \approx 200$ ns, the electric field strength was the same for both pulses. At small electric fields the amplitude of the echo is expected to rise proportional to F_0^3 . It reaches a maximum at a field fulfilling the condition $\Omega t_{p2} \approx \pi$ for the second pulse. At higher electric fields the shape of the echo starts to change, splitting eventually into different negative and positive parts.¹⁸ In this regime it is not obvious which maximum one should take as the echo amplitude. Therefore, we have decided to plot always the integrated echo amplitude, because this is a well-defined quantity even at large fields. After passing through the maximum the integrated echo amplitude is expected to decrease towards higher fields, since in this range the signal consists of negative and positive components.

In Fig. 2 the integrated amplitude of two-pulse polarization echoes generated in BAS at different magnetic fields is plotted as a function of the applied electric field strength. All curves show the expected variation with the electric field strength, but the absolute value of the echo amplitude is different at different magnetic fields. It is noteworthy that the echo amplitude is a non-monotonic function of the applied magnetic field. The fact, that independent of the applied magnetic field the maximum of the integrated echo amplitude is always found at the same electric field strength of about 450 V/m indicates that the mean effective Rabi frequency remains virtually unaltered in magnetic fields. From this we conclude that neither the dipole moment p nor the tunneling splitting Δ_0 depend on the applied magnetic field. This observation disfavors the model proposed by Kettemann et al.⁶ as an explanation for the magnetic field dependence of the echo amplitude.

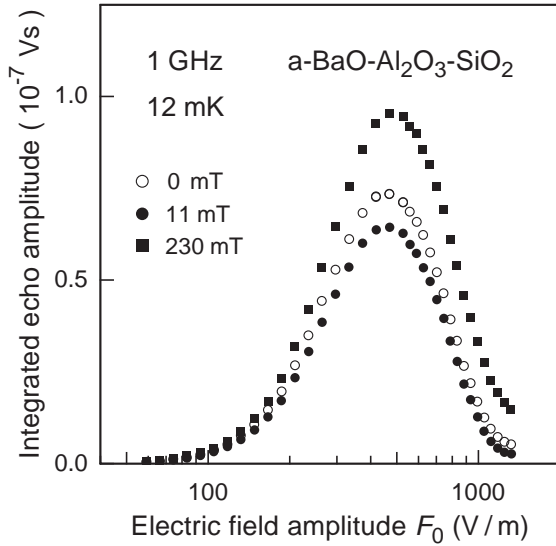


FIG. 2: Electric field dependence of the amplitude of the spontaneous polarization echo in BAS at zero field, 11 mT and 230 mT (from reference 8).

2. Material Dependence

We have studied the coherent properties of four different glasses in magnetic fields in order to investigate the material dependence of the magnetic field effects. The amplitude of two-pulse polarization echoes of these four glasses is shown in Fig. 3 as a function of magnetic field.²⁹ In contrast to many other low-temperature properties of glasses the influence of magnetic fields on the amplitude of spontaneous echoes is obviously not universal. Several conclusions can be drawn from the results shown in Fig. 3. The occurrence and the magnitude of the magnetic field dependence is independent of the concentration of magnetic impurities present in the glass samples. In particular, BK7 and Duran show similar effects although the concentration of magnetic impurities differs by at least a factor of 20 as demonstrated by the magnetization measurements shown in Fig. 1.

Perhaps the most remarkable result of the measurements plotted in Fig. 3 is the fact that Suprasil I shows no magnetic field effect within the accuracy of our experiment. The slight difference between positive and negative fields is caused by drift problems in the experiment. Whereas Duran, BAS and BK7 contain isotopes with non-zero nuclear quadrupole moment, Suprasil is virtually free of such isotopes.³⁰ This strongly indicates that nuclear quadrupoles play a crucial role in the magnetic field effects, and therefore, our result clearly favors the nuclear quadrupole model.⁹

The variation of the echo amplitude with applied magnetic field is similar for Duran, BK7 and BAS, but not identical. All three samples exhibit a central maximum at $B = 0$. At high fields the amplitude of the echo rises above its value at zero magnetic field and seems to reach saturation at fields above 200 mT. Fig. 4 shows the vari-

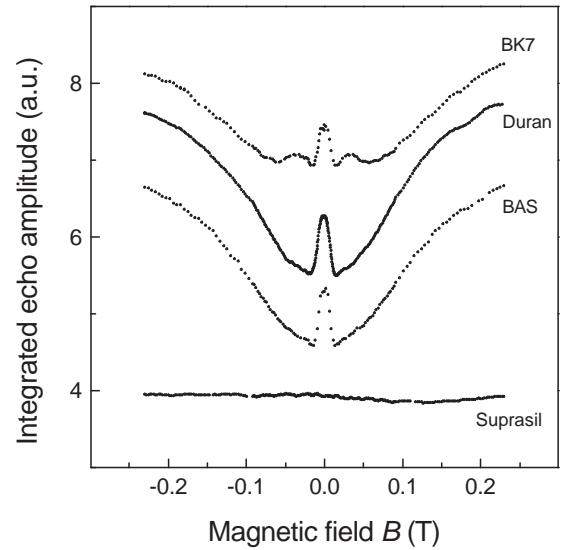


FIG. 3: Magnetic field dependence of the amplitude of spontaneous polarization echoes in BK7, BAS, Duran, and Suprasil I. All data were taken at 12 mK, $t_{12} = 2 \mu\text{s}$ and roughly 1 GHz, except that for Duran, where the delay time was $t_{12} = 1.7 \mu\text{s}$.

ation of the echo amplitude for BAS at $t_{12} = 1 \mu\text{s}$ in an extended field range. In this plot the saturation effect becomes evident. According to the nuclear quadrupole model this saturation occurs at magnetic fields at which the nuclear Zeeman energy exceeds the mean quadrupole splitting. This condition seems to be met roughly at the same magnetic field in all three glasses (see Fig. 3), although the relevant nuclei are probably either ^{11}B or ^{27}Al with different nuclear quadrupole moments.

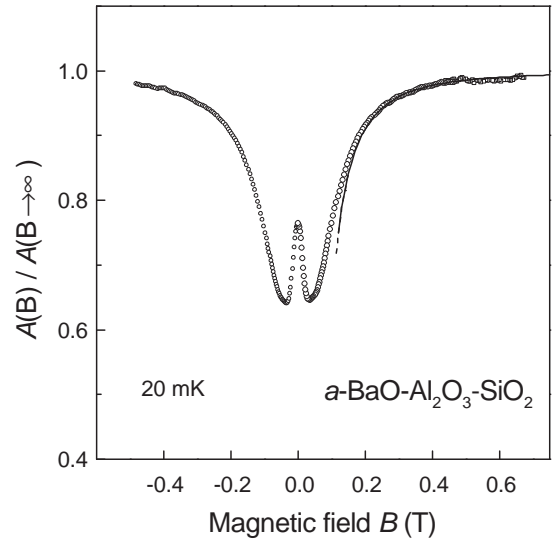


FIG. 4: Amplitude of spontaneous polarization echoes in BAS in magnetic fields up to 0.7 T. The data were taken in at 1 GHz, 20 mK and $t_{12} = 1 \mu\text{s}$. The solid line represents the expected variation at high fields according to the quadrupole model.

The solid line in Fig. 4 represents the prediction (11) of the quadrupole model for large fields with $B_0 = 60$ mT as fitting parameter. It describes the high field limit almost perfectly. From the value of B_0 we deduce the Larmor frequency $\omega_L = 4.2$ MHz for the aluminium nuclei. Assuming further that $\hbar\omega_L \approx \hbar\omega_Q$ at B_0 , we obtain for the electric field gradient the value 8×10^{20} Vm $^{-2}$ which is of the right order of magnitude.

3. Delay Time Dependence

Further remarkable observations were made in measurements of the magnetic field dependence of the amplitude of two-pulse echoes with different delay times t_{12} between the exciting pulses. As an example, we show in Fig. 5 the amplitude of spontaneous echoes excited in BK7 as a function of the applied magnetic field for different delay times. The pattern of the magnetic field dependence is clearly different for different values of t_{12} . This observation indicates that the applied magnetic field influences the free phase development of the tunneling systems between and after the two excitation pulses.

This can be made even more obvious by plotting the amplitude as a function of the product of the magnetic field and the delay time t_{12} . Fig. 6 shows such a plot for the data displayed in Fig. 5. It is remarkable that several features of the curves at different delay times coincide in this representation. In particular, the width of the central maximum in this plot is nearly identical in all cases. In addition, we have marked two features by dashed lines, the minimum at negative fields and the second maximum at positive field strength. Such an invariance of the pattern with respect to the product Bt_{12} is expected in the quadrupole coupling model at small magnetic fields. According to this approach, mixing between nuclear levels

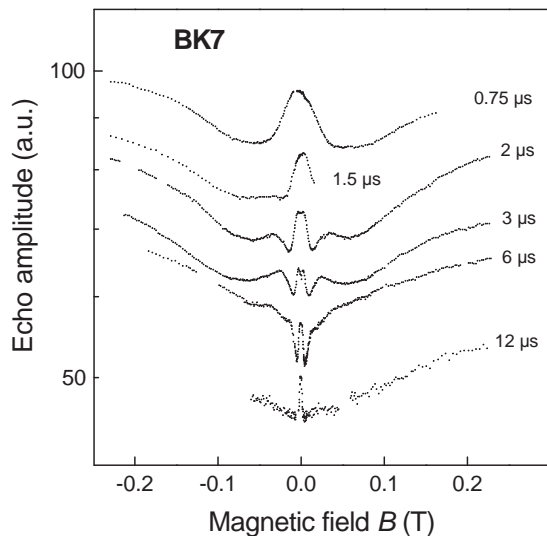


FIG. 5: Amplitude of two-pulse echoes generated in BK7 as a function of magnetic field at different delay times. All data sets were taken at 4.6 GHz and 12 mK except that for $t_{12} = 2 \mu\text{s}$ which was taken at 0.9 GHz.

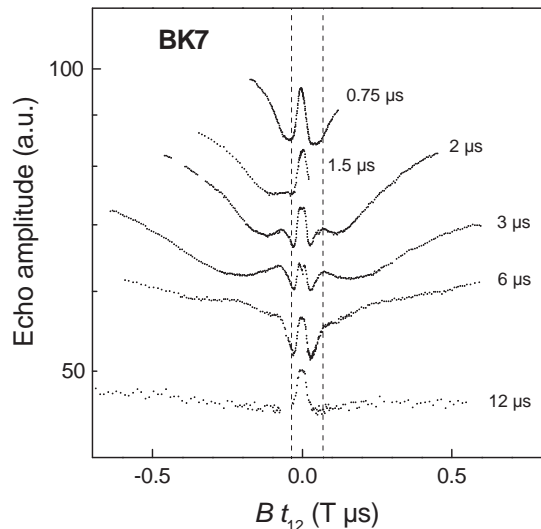


FIG. 6: Amplitude of two-pulse echoes generated in BK7 as a function of the product of the magnetic field B times the delay time t_{12} . The dashed lines mark the positions of typical features of the echo amplitude.

is the cause of these features. From the data shown in Fig. 3, the first minimum is observed at about 14 mT in all three glasses. In BK7 the two boron isotopes ^{10}B and ^{11}B as well as sodium are likely to cause the magnetic field effect (see Table II). In the case of BAS the main contribution is probably due to ^{27}Al nuclei. Using the rough approximation (10) and the appropriate g -factors we deduce values of about 11 mT for the minima in fair agreement with our observations. Applying (10) to the lighter boron isotope ^{10}B leads to a greater value of the magnetic field at the minimum. However, it is not clear whether (10) is applicable since a theory for the contribution of integer spins is still lacking.

The absence of a second maximum in case of Duran and BAS (Fig. 3) is another interesting observation made in our experiments. In the light of the quadrupole coupling model this might be caused by the larger amount of magnetic impurities in these materials compared to BK7, because it is conceivable that electronic spins lead to a distribution of local magnetic fields and therefore might wash out certain interference patterns.

Despite the good qualitative and partially even quantitative agreement of the quadrupole coupling model we want to point out that not all details of the curves shown in Fig. 5 can be described by (9).

4. Frequency Dependence

A pronounced frequency dependence of the magnetic field effects in polarization echo experiments is expected from both models assuming a direct coupling of magnetic fields to tunneling systems.^{6,7} Fig. 7 shows the magnetic field dependence of the echo amplitude of BK7 measured at 0.9 GHz and 4.6 GHz, and at two different delay times. Note that the magnetic field is plotted on a logarithmic

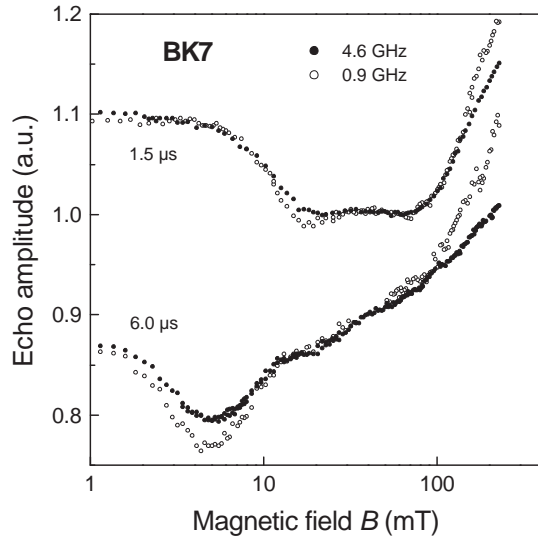


FIG. 7: Amplitude of two-pulse echoes generated in BK7 as a function of magnetic field at two different frequencies and at two different delay times.

scale. Again, the curves at different delay times exhibit a different pattern as a function of the applied magnetic field, but hardly any frequency dependence is seen within the accuracy of the experiment, although frequencies differ by a factor of five. The remaining differences between the curves in particular at the long delay time of $6\mu\text{s}$ and at higher magnetic fields could be caused by experimental problems.

The apparent absence of a frequency dependence in this experiment provides further evidence that the models favoring a direct coupling of magnetic fields to tunneling systems are not applicable in this case. In contrast, no (strong) variation with measuring frequency is expected within the nuclear quadrupole coupling model, because the relevant energy scales are given by the nuclear properties of the tunneling systems.

5. Temperature Dependence

If the nuclear quadrupole model is the correct description, the magnetic field effects observed in the two-pulse echo experiments are expected to be temperature independent because of their pure quantum nature. We have studied the temperature dependence of the magnetic field effects of two glasses: Duran and BAS. The result for Duran is shown in Fig. 8 where the integrated echo amplitude is plotted on a logarithmic scale. With rising temperature the amplitude of the echo decreases strongly. However, the pattern of the magnetic field variation remains nearly unaltered. There is a small decrease of the magnetic field variation relative to the absolute echo amplitude, which is hardly visible in this representation.

The magnetic field dependence of the echo amplitude in BAS at 20 mK and 56 mK is shown in Fig. 9 where the normalized amplitude $A(B)/A(B \rightarrow \infty)$ is plotted

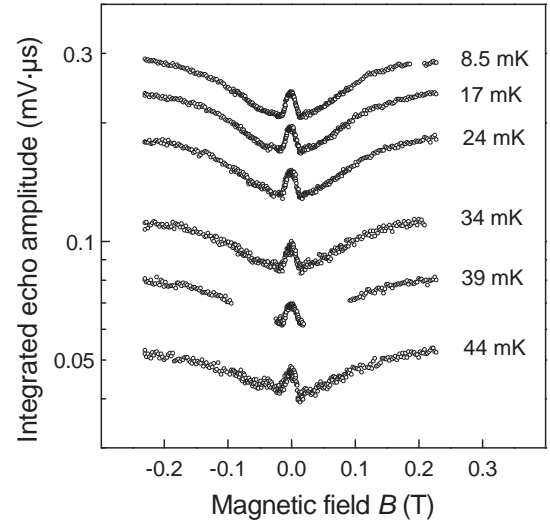


FIG. 8: Amplitude of two-pulse echoes generated in Duran as a function of magnetic field at different temperatures. In this experiment the microwave frequency was roughly 1 GHz and the delay time $1.7\mu\text{s}$.

on a linear scale. As in the case of Duran, the overall pattern remains unchanged as the temperature increases although the relative variation is larger at the lower temperature. With rising temperature the magnetic field effect vanishes obviously more rapidly than the amplitude of the echo itself. At a first glance this is unexpected from the point of view of the quadrupole model. In an attempt to explain this finding we may distinguish between tunneling particles with and without nuclear quadrupole moment. In both cases, the temperature dependence of the

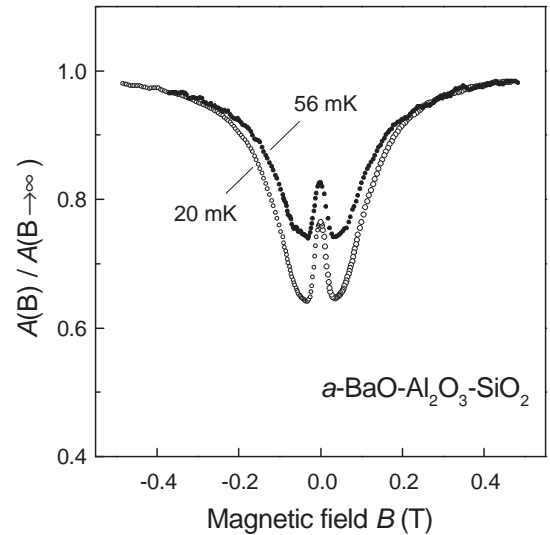


FIG. 9: Amplitude of two-pulse echoes generated in BAS as a function of magnetic field at two different temperatures. The measurement was performed about 1 GHz and a delay time of $1\mu\text{s}$. In both cases the echo amplitude is normalized to its value at high fields.

echo amplitude is assumed to be independent of magnetic fields. However, it is conceivable that the temperature dependence of the dephasing time of systems carrying a nuclear quadrupole moment is different from that of systems without a nuclear quadrupole moment. In this case the magnitude of the magnetic field effect would also depend on temperature.

Finally we want to add that the decay of spontaneous echoes in glasses is much faster than expected.³¹ According to theory¹⁷ the decay is due to spectral diffusion and is consequently determined by the thermal relaxation of tunneling systems with an energy splitting $E \approx 2k_B T$. In this context one might speculate whether a novel, hitherto unconsidered mechanism gives rise to fast relaxation because of the more complex level scheme of tunneling systems with a nuclear quadrupole moment.

V. SUMMARY AND OUTLOOK

We have measured the amplitude of the two-pulse echoes generated in four different glasses in magnetic fields. Three glasses exhibit a striking non-monotonic magnetic field variation, but vitreous silica Suprasil I shows no magnetic field effect. From the absence of this phenomenon in Suprasil I, and from the influence of other parameters, such as delay time, electric field, temperature, and frequency on the magnetic field effect we conclude that tunneling particles carrying a nuclear quadrupole moment are responsible for the surprising phenomena. The nuclear quadrupole of these systems

leads to a splitting of the nuclear spin levels even at zero magnetic field, which is different for the ground state and the excited state. The presence of this multi-level structure reduces the echo amplitude compared to that of simple two-level systems. As long as the Zeeman energy is smaller than the mean quadrupole splitting, mixing between the nuclear spin levels leads to a non-monotonic variation of the echo amplitude with the magnetic field. At a large magnetic field the Zeeman effect is dominant and the echo amplitude saturates at the value expected for simple two-level systems.

We believe that nuclear quadrupoles also play an important role in other experiments on glasses at low temperatures. For example the magnetic field dependence of the dielectric susceptibility at low frequencies is likely to be caused by relaxation effects involving nuclear spin levels. In addition, we like to point out that the fact that the nuclear properties of the tunneling particles matter, might allow to study the microscopic nature of the tunneling systems in glasses by investigating glasses of selected composition.

Acknowledgment

We thank R. Weis, A. Würger, P. Strehlow for many stimulating discussions. In particular, we acknowledge the help of B. Renker in the measurement of the impurity concentration of BK7 and Duran. This work was supported by the Deutsche Forschungsgemeinschaft.

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until now no theory has been worked out for nuclei with integer spin.

²⁶ For a general discussion of dephasing in multi-level systems see J.J. Yeh, J.H. Eberly, Phys. Rev. A **22**, 1124 (1980).

²⁷ In the nuclear quadrupole model, this problem has been worked out in more detail. In fact, the structure of the minimum is more complex because of the contribution of the different Zeeman levels. In addition, the exact position of the minimum depends on the distribution function $p(x)$.

²⁸ The analysis was carried out at the Fraunhofer-Institut für Silikatforschung in Würzburg. We thank P. Strehlow

for making these results available to us.

²⁹ If not stated differently, the echo amplitudes were multiplied by different arbitrary factors in order to obtain a unified representation of the data.

³⁰ The only isotope with non-zero nuclear quadrupole in pure Suprasil I is ^{17}O ($I = 5/2$) which has a natural abundance of only 0.05%.

³¹ See for example, C. Enss, Adv. Solid State Phys. **42**, 335 (2002).